

PATENT SPECIFICATION

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Date of Application and filing Complete Specification: April 18, 1962.

No. 15078/62.

Application made in Germany (No. A37219 IXa/57b) on April 19, 1961.

Application made in Germany (No. A38942 IXa/57b) on Dec. 5, 1961.

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COMPLETE SPECIFICATION

Process for Developing Electrostatic Latent Images

SPECIFICATION NO. 987.766

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are Wolf Gesierich, Lorzling-Strasse 22, Leverkusen, Germany; Edith Weyde, 3 Von Diergardt Strasse, Leverkusen, Germany; Hildegard Haydn, Walter-Flex-Strasse 6, Leverkusen, Germany; all of German Nationality.

THE PATENT OFFICE

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quartz sand. When these mixtures are used, it is necessary to heat the image by heating the image until the pigmented resin particles fuse on the support.

15 It is also known to develop a latent electrostatic image by spraying with dyed aerosols, the charged zones on the electrophotographic material being coloured. The liquid which is dried or absorbed thereon then produces the stable image. According to an embodiment of these processes the aerosol is charged electrostatically for example by means of a high voltage installation, and is sprayed into the electrical field of an electrode system in which the electrophotographic material constitutes an electrode. Furthermore the electrophotographic layer can be developed in the corresponding manner with uncoloured liquid mists. In these cases, the liquid image is transferred to a second image support and is made visible on the latter by means of soluble dyestuffs.

25 According to other known processes, the surface which is charged according to an image is developed with a developer liquid.

The known processes can be improved by the deposition of the developer liquid being controlled by means of an electric field, which is set up between the electrophotographic material bearing the latent electrostatic image and an electrode facing this layer. Such an arrangement is particularly necessary for aerosol development.

30 For the developing methods which are based on electrophoretic principles the developing liquids consist of a dispersion of the colour - supplying component in a neutral organic liquid with high electrical resistivity and low dielectric constant. Suitable liquids include kerosene, turpentine, benzene or carbon tetrachloride; they are selected because of their high resistivity, a property which is essential to avoid discharge of the latent electrostatic image. The coloured or colour - supplying developer particles dispersed in said insulating liquid have as regards their electric properties to meet the condition that their relaxation time is far greater than the developing time. In many cases, the liquid developers also have added thereto artificial or natural resins, which impart a charging opposite to the latent image to the dispersed colouring particles or by means of which the pigment is fixed on the image support when the liquid medium has evaporated. In the use of these developers the development is accomplished by the aid of an electric field between two electrodes one of which is the electrophoto-

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COMPLETE SPECIFICATION

Process for Developing Electrostatic Latent Images

We, AGFA AKTIENGESSELLSCHAFT of Leverkusen Bayerwerk, Germany, a Body Corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of electrophotographic images, using liquid developers.

The principle of the known electrophotographic processes consists in that a latent, electrostatic charging image is produced by image-wise exposure of a charged photoconductive layer, which image is then developed by a developer in liquid or powder form which is precipitated according to the charge on the photoconductive layer, to form a visible image. The known powder developers consist of particles of fusible resins, which contain pigments such as carbon black and of carrier materials such as quartz sand. When these mixtures are used, it is necessary to fix the visible image by heating the image until the pigmented resin particles fuse on the support.

It is also known to develop a latent electrostatic image by spraying with dyed aerosols, the charged zones on the electrophotographic material being coloured. The liquid which is dried or absorbed thereon then produces the stable image. According to an embodiment of these processes the aerosol is charged electrostatically for example by means of a high voltage installation, and is sprayed into the electrical field of an electrode system in which the electrophotographic material constitutes an electrode. Furthermore the electrophotographic layer can be developed in the corresponding manner with uncoloured liquid mists. In these cases, the liquid image is transferred to a second image support and is made visible on the latter by means of soluble dyestuffs.

According to other known processes, the surface which is charged according to an image is developed with a developer liquid.

The known processes can be improved by the deposition of the developer liquid being controlled by means of an electric field, which is set up between the electrophotographic material bearing the latent electrostatic image and an electrode facing this layer. Such an arrangement is particularly necessary for aerosol development.

For the developing methods which are based on electrophoretic principles the developing liquids consist of a dispersion of the colour-supplying component in a neutral organic liquid with high electrical resistivity and low dielectric constant. Suitable liquids include kerosene, turpentine, benzene or carbon tetrachloride; they are selected because of their high resistivity, a property which is essential to avoid discharge of the latent electrostatic image. The coloured or colour-supplying developer particles dispersed in said insulating liquid have as regards their electric properties to meet the condition that their relaxation time is far greater than the developing time. In many cases, the liquid developers also have added thereto artificial or natural resins, which impart a charging opposite to the latent image to the dispersed colouring particles or by means of which the pigment is fixed on the image support when the liquid medium has evaporated. In the use of these developers the development is accomplished by the aid of an electric field between two electrodes one of which is the electrophoto-

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graphic material or a metal plate on which the electrophotographic material is arranged. The colour component dispersed in the high insulating developer liquid is transported in said electric field to the latent electrostatic image of said electrophotographic material forming thereby a visible image. In this case in the course of the development a change of the concentration of the coloured developer particles dispersed in the developing liquid occurs in such a way that the coloured particles are concentrated in the vicinity of or on the electrophotographic layer. The liquid of the developer acts only as carrier medium for the coloured particles and does not actively take part in the development.

The known processes have disadvantages in many respects, so that the use thereof in practice is questionable. The organic support liquids which can be used are generally combustible and physiologically are not unobjectionable. In order to prevent injury to the personnel working with these developers, it is consequently often necessary to provide extensive protective measures. An additional disadvantage is that these organic liquids act as solvents or plasticisers on the electrophotographic materials. This is especially the case with those liquid developers which contain resin additives in dissolved form for the better fixing of the developed image. Moreover, the organic developer liquids are partially lost with the development. Thus, these developing processes are also often very uneconomic.

In developing methods working according to electrolytic principles also transport of the coloured developer particles and change of concentration of said particles in the developer liquid occurs in the course of development. The developer liquids consist generally of a solution of the coloured or colour - supplying component in a suitable solvent. The liquid acts only as a carrier medium for the developer particles and does not actively take part in the development.

The electrolytic developing processes are disadvantageous in many respects. The developing times are too long since the electrolytic deposition of the developing particles requires times of minutes. Furthermore in this process a final drying of the electrophotographic materials is necessary since they absorb developer liquid. The electrophotographic materials suitable for this process have to contain a layer of a conductive metal e.g. aluminium.

Summarising, it can be established that the processes referred to are characterised by the relatively high cost of carrying them out and by considerable practical disadvantages.

It is among the objects of the instant invention to avoid the disadvantages described above and to provide a simple and inexpensive technique for developing electrostatic images. The developing method according to the invention makes use of a physical phenomenon which hitherto was not used in connection with electrophotographic processes. The new process is characterized by the term "wetting development."

~~It has now surprisingly been found that an electrophotographic layer which is~~
~~imagewise charged is wetted according to the charging on contact with water or~~
aqueous liquids. The wetting takes place at those places on the layer which carry charges, whereas uncharged zones remain unwetted. The image formed in this way and consisting of water is visible in incident light, because of different light refractions or reflection of wetted and unwetted areas. If the aqueous liquid is a solution or a dispersion of a dyestuff, a dyestuff image is formed in the same manner, which image can either be left to dry on the support or can be transferred by printing to a second support in known manner while still moist.

The present invention, therefore provides a process for the production of electrophotographic images wherein a supported photoconductive layer is charged and exposed to an object so as to form a latent electrostatic image which is developed by bringing the entire layer into contact with an aqueous developer composition having electric and wetting characteristics such that the charged areas are wetted by the composition while the uncharged areas repel it.

The aqueous developers suitable for the process according to the invention have to meet the following conditions:

The difference of the wetting angle between the light - struck and nonlight-struck areas respectively the charged and the uncharged areas of the exposed electrophotographic layer should be as great as possible whereby the wetting angle at those areas of the latent electrostatic image not to be wetted should be greater than 90° and at those areas to be wetted smaller than 90° . The wetting angle can be measured according to known methods or can be estimated in usual manner from the surface energies according to the Young - equation. The magnitude of the surface energy at a liquid-gas,

liquid-liquid or liquid-solid interface is closely related to the surface tension of the liquid on that interface.

The Young equation is:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos \alpha$$

$$\text{or } \cos \alpha = \frac{\sigma_s - \sigma_{sl}}{\sigma_l}$$

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σ_l

σ_{sl} = interfacial tension

solid/liquid

σ_s = " "

solid/gaseous

σ_l = " "

liquid / gaseous

α = wetting angle

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It follows for the wetting conditions:

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non-wetting: $\alpha \geq 90^\circ$, $\cos \alpha < 0$, $\sigma_s < \sigma_{sl}$

wetting: $\alpha \leq 90^\circ$, $\cos \alpha > 0$, $\sigma_s > \sigma_{sl}$

The most important electric property of the aqueous developer is the "relaxation time" i.e. the time necessary for the displacement of charges inside the developer drop or developer film under the influence of an electric field. The relaxation time should be small as compared with the developing time. If so, the aqueous developer has to be considered as conductive. The relaxation time can be estimated from the following equation

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$$\tau = \epsilon \cdot \epsilon_0 \cdot \rho \quad [\text{sec.}]$$

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In this equation τ represents the relaxation time of the developer, ϵ_0 the absolute dielectric constant, ϵ the dielectric constant of the aqueous developer and ρ the resistivity of the aqueous developer. Hence it follows that the relaxation time can mainly be influenced within wide limits by varying the conductivity of the developer liquid. Aqueous developers having a resistivity smaller than 10^6 Ohm. cm. are suitable for the wetting development.

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Aqueous developers suitable for the process according to the invention include solutions or dispersions of coloured compounds or compounds capable of yielding coloured products by subsequent chemical reaction. Suitable coloured products are for example (the numbers in parentheses represent the numbers of the corresponding dyestuffs in the 7th edition of the Schultz dyestuff tables);

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Water-soluble *azo* dyestuffs, such as Azofuchsin B (80), Ehtrot BT (122), Benzogrün C (688), Bismarckbraun (311), Naphthylamin 10 B (299), ~~Vibronschwarz E (587); triarylmethane dyestuffs, such as Melachinon (754), Kristallviolett (785), Säurefuchsin (800), Türkisblau BB (757); diphenyl methane dyestuffs, e.g. Auramin G (753); stilbene dyestuffs, such as Diphenylorange RR (710) or Brillantgelb (724); pyrazolone dyestuffs, such as Echtlichtgelb G (732), Tartrazin (737); xanthene dyestuffs, such as Rhodamin 5 G (862) Säureviolett 4R (871), Eosin (881), Erythrosin (866), Phloxin (888), Rose Bengal (889,891); acridine dyestuffs, e.g. Acridingelb (901) or Acridinorange (902); quinoline dyestuffs, such as Chinolingelb (918); quinonimine dyestuffs, such as Tolylenblau (937), Hansagrün (940); thiazine dyestuffs, e.g. Methylenblau (1038), Methylengrün (1040), thiazole dyestuffs, e.g. Primulingelb (932); azine dyestuffs, e.g. Indulinscharlack (947), Phenosafranin (958), nigrosin (986); oxazine dyestuffs, such as Coelestinblau B (1015); sulphur dyestuffs, such as Thiongrün B (116).~~

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It is also possible to use coloured water - soluble simple compounds or complexes. such as form a number of transition elements, primarily of the first long period of the Periodic System, for example the known cuprous tetrammine complex, chromium salts such as chromic sulphate, potassium chrome alum, potassium chromate, compounds known as ammine, aquo and acido complexes of trivalent chromium, potassium permanganate, ferric compounds, such as ferric thiocyanate and the thiocyanato ferrates i.e. compounds containing the anion $[\text{Fe}(\text{SCN})_6]^{3-}$, soluble Berlin blue $\text{KFe}[\text{Fe}(\text{CN})_6]$, the ferricyanides, acetate complexes of ferric salts, iron - ammonium citrate, the thiocyanate and the thiocyanocobaltates of divalent cobalt i.e. compounds containing the anion $[\text{Co}(\text{SCN})_6]^{2-}$, cobaltous sulphate, and chloride, the large number of cobaltic complexes, for example the amine, aquo and acido complexes, which exist in similar

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abundance to those of the chromic complexes, chlorides and sulphate of divalent nickel, the copper tartrate complex, copper glycine, the soluble compounds of iron and gallic acid or tannin, the complexes of the ferrous salts with α -picolinic acid or homologous compounds which contain a cyclically combined nitrogen atom in the α -position to a carboxyl group, the complexes of divalent iron or cobalt with α -dioximes, such as dimethyl glyoxime, the ferric complexes with salicylic acid, the compounds of titanium or iron salts and pyrocatechol or chromotropic acid.

Since aqueous solutions as well as dispersions of preferably coloured compounds can be used as developer liquids for the developing process according to the invention it is easily possible to select a suitable compound from the large number of available coloured products. It should be expressly pointed out that the chemical structure of the coloured compound is not especially critical and that the compound is selected according to the requirements of the reproduction process in which the developer is to be used.

It is apparent from what has been shown above that all water-compatible colouring compounds are suitable for the present purpose.

According to another embodiment of the invention the development can be accomplished with colourless aqueous solutions if the developer has dissolved therein substances which supply coloured products by a chemical reaction.

Many different types of reactions can be used for this process. For example, the aqueous developer can have added thereto substances which show a change in colour with alteration of the pH-value. In principle, this group of substances includes all compounds which are used in known manner as indicators. It is preferred to use those substances which *per se* are colourless and change into a coloured form with a change in the pH-value. The substance is all the more suitable in proportion as the corresponding coloured product is more intensively and deeply coloured. It is also possible to use reduction reactions or exchange reactions which lead to the formation of coloured inorganic or organic compounds. In practice, it is possible to employ all reactions which are known from analytical chemistry and serve for detecting certain cations or anions, for example the formation of coloured metal sulphides.

Coupling reactions which use diazonium compounds and which lead to the formation of coloured products are especially suitable.

The possibility of using chemical reactions for the coloured development of electrophotographic images with the use of developers in powder form is already known. In contrast hereto, the process according to the invention does however have considerable advantages. Thus, the choice of suitable reactants is substantially simpler, since in the present case the only condition as regards whether they can be used is the compatibility with water of at least one reactant and the formation of a reaction product of deepest possible colour. With the known developers, on the other hand, as well as the properties necessary for the chemical reaction, it is also necessary to observe the electrostatic or triboelectric properties necessary for a developer in powder form. Furthermore, in these cases, additional steps such as for example moistening, heating and the like are usually also necessary for initiating the colour reaction.

The reaction components for the colour - yielding reaction can be introduced in various ways. The simplest possibility of reaction is provided by incorporating one of the components in the electrophotographic layer, the other component being dissolved in the developer. Reaction between the two will then take place only in those regions of the electrophotographic material, that are wetted according to the process of the invention by the aqueous developer. With this form of the process, the component in the electrophotographic layer which reacts with the developer solution can be chosen to act simultaneously as sensitiser for the photo - conductor or it can even itself be the photo-conductive substance.

It is also possible to dissolve two colourless substances in the developer, which substances only participate in a reaction with formation of a coloured product upon contact with the electrophotographic layer.

Furthermore, when using conventional electrophotographic materials containing no additional substances, one of the reaction components can be dissolved in the developer, be developed in the manner according to the invention and thereafter the colour formation can be achieved in an additional working step by treatment with a liquid or gaseous reaction component.

The above statements illustrate that the development process according to the invention is capable of being varied in many ways. The choice of a specific colour

reaction will depend substantially on the nature of the other materials actually being used.

It has proved to be advantageous that the image-wise charged electrophotographic image is not dipped into the aqueous developer but is merely brought into contact with the surface of the aqueous developer. According to a preferred embodiment the development is achieved by moving the electrophotographic material containing the latent electrostatic image over a film of the developer liquid in such a manner that one section of the surface after the other is wetted by the liquid film. The liquid film should with advantage be screened. Various possibilities exist for the production of such a liquid screen. Thus, the liquid level can be covered with a fine-mesh, non-absorbing fabric, consisting for example of polyamides. The developer liquid will then be brought into contact with the surface of the image-wise charged electrophotographic layer through the meshes of the fabric and wet the said layer according to the charging. By using a screen-like fabric a uniform application of the aqueous developer is simultaneously obtained. Furthermore it is possible to achieve a weaker or stronger application of the possibly coloured developer liquid by varying the force with which the electrophotographic layer is pressed onto the fabric wetted with the developer. Instead of the fabric which has been described, it is also possible to use devices or rollers provided with a roughened screen-like surface.

These devices should consist of materials which are wetted by the developer liquid without however absorbing the said liquid. Furthermore, a certain elasticity is necessary so that the liquid level can be adapted to the surface of the electrophotographic layer bearing the latent electrostatic image.

Synthetic plastics are therefore especially suitable for these devices. The developing apparatus should preferably contain devices or means for storing a sufficient quantity of developer. This can be achieved for example by a sand cushion saturated with the developer liquid. Furthermore, it is possible to use roller systems such as those known for use in the printing industry. In this case, the applicator roller provided with a screen-like notched pattern is supplied with the necessary liquid by means of a second roller from a developer storage container.

The liquid image is generally absorbed into the microscopically small irregularities of the surface of the image support thus producing an image which cannot be wiped off. In cases which make it desirable to have a particularly high mechanical resistance of the image, the developer solution can contain adhesive or thickening agents added thereto without any disadvantages as regards the quality of the developed image, for example gum arabic, agar-agar, tragacanth, dextrans, guar, (a polysaccharide comprising 65% of mannose units and 35% of galactose units) carrageenates (i.e. salts of carrageenin), cellulose derivatives such as esters or ethers, alkali metal salts or esters of alginic acid, polyvinyl alcohol, polyvinyl pyrrolidone and polyvinyl carbazole. The properties of the aqueous developer can be modified by the addition of alcohols such as glycols, glycerol or polyethylene oxides.

By comparison with the known development processes, the process according to the invention has numerous advantages. In addition to economy, there is especially to be mentioned the safe handling of the aqueous solution. Furthermore, a charging of the developer such as is necessary with the various forms of aerosol development is superfluous. The electrophotographic images which are obtained are superior as regards quality to those produced by the known development processes. Since no pigment particles are deposited, the images are without grain and very sharp, so that these images can be greatly enlarged. The liquid is absorbed by the support in a manner similar to ink, so that a separate fixing, as for example with the various powder processes, is unnecessary. The process according to the invention also makes it possible for development with different colours to be carried out in succession.

In order that the invention may be more clearly understood the following Examples are given by way of illustration only:—

EXAMPLE 1

320 g. of organopolysiloxane resin (for example Type Bayer P 150 which contains methyl and phenyl groups), 60% in toluene, 500 g. of toluene and 450 g. of chemically pure, photoconducting zinc oxide are ground for about 3 hours in a ball mill, thereafter cast on to paper and dried. The electrophotographic paper thus produced is electrostatically charged by means of a corona discharge device and exposed to form an image. For the development of the latent charging image, a filtered solution of 500 mg. of Kristallviolett in 10 ml. of water is used. The electrophotographic image support is for this purpose tensioned on a roller with a thickness of

about 10 cm. and rolled over a sand surface which is formed into a paste with the dyestuff solution and which is spread out flat and doctored. The grain size of the sand is between 25 and 50 μ . A sharp, practically grainless, violet colour image is obtained, which adheres after a few seconds to the support in such a way that it cannot be wiped off.

EXAMPLE 2

The same material as in Example 1 is used. The latent image is developed in the manner described with a 3% aqueous potassium permanganate solution. After drying, a vigorous brownish image is obtained.

EXAMPLE 3

300 g. of a product which has been prepared by vacuum esterification of 2 mols of phthalic acid anhydride, 1 mol of adipic acid, trimethylol propane and subsequent reaction with 4.8 mols of cyclohexyl isocyanate are dissolved in 1000 g. of acetic ester. 670 g. of photoconductive zinc oxide are then added and the mixture is shaken for 2 hours on a vibratory mill, cast on to baryta - coated paper and dried. An electrostatic charging image is produced on the layer by known methods. In order to make the image visible, a developer liquid prepared by dissolving 100 mg. of Rose Bengal in 20 ml. of water is applied by means of a roughened steatite roller. The surface structure of the roller has an average spacing of the irregularities of about 10 to 500 μ with a depth of 30 to 100 μ .

EXAMPLE 4

A mixture of 140 g. of photoconductive zinc oxide 120 g. of alkyd resin (a condensation product of trimethylol propane and phthalic anhydride with added soy oil), 320 g. of toluene and 10 g. of cobalt naphthenate solution (10% in toluene) is applied to aluminium lined paper and dried. The development of the charged layer exposed to form an image is effected with an aqueous solution of Papiertiefschwarz AGX (Colour Index No. 20470 Trade Name of Farbenfabriken Bayer) which contains 1.5 g. of dyestuff to 300 ml. of water. The dyestuff solution is applied by means of a rubber roller, which is covered with Perlon (a Registered Trade Mark) mesh fabric. The mesh fabric has a thickness of about 50 μ and a mesh size of about 25 μ . A deep black image is obtained.

EXAMPLE 5

The electrophotographic material described in Example 4 is used. The liquid used for the development consists of a solution of 11.5 g. of tannin, 3.8 g. of crystallised gallic acid, 15 g. of ferrous sulphate, 5 g. of 25% hydrochloric acid, 0.5 g. of phenol and 5 g. of gum arabic, in 500 cc. of water. The electrostatic charging image is produced according to Example 4 and made visible, and immediately after ~~completing the developing process, it is transferred to normal writing paper~~ A copy of the original corresponding exactly to the document is obtained.

EXAMPLE 6

200 g. of white, photoconductive zinc oxide are dispersed in 300 g. of a 35% solution of polystyrene in toluene by means of a high - speed mixer, cast on to an acetyl cellulose film vapour - coated with aluminium and dried. The latent charging image produced on the layer is developed with the aid of 10% aqueous iron-ammonium citrate solution. For this purpose, the image support is pressed on to a cushion, the cover of which consists of a nylon fabric with a mesh size of on average 200 μ and filled with polystyrene beads with a size of 300 to 400 μ . On stripping off the image support an image of rusty brown colour is obtained.

EXAMPLE 7

The material described in Example 6 is used. As developer liquid, there is employed a clear solution of 14 g. of 80% tannin, 3.5 g. of crystallised gallic acid, 15 g. of 15% FeCl_2 solution, 4 g. of hydrochloric acid (1.16), 2.5 g. of naphthol-blauschwarz (Colour Index No. 20470), 0.5 g. of phenol in 500 g. of water. A bluish black image is obtained.

EXAMPLE 8

100 g. of chemically pure photoconductive zinc oxide (Merck p.a.), 30 ml. of silicone resin, 60% in toluene (for example silicone resin Bayer P 150) and 100 ml. of toluene are introduced into a ball mill (capacity 1 litre), which is half filled with porcelain balls (1.5 cm. diameter). The mixture is ground for 2 hours and thereafter applied by means of an applicator roller to document paper (100 g./m²) and dried. The thick-

ness of the layer is about 15 μ . The material is electrostatically charged at 7 kV by means of a corona discharge device, exposed image-wise by means of an incandescent lamp and developed as follows.

5 For preparing the developer, the ultra-fine fraction of the normal commercial quality of carbon black is formed into a paste with concentrated nitric acid, diluted with distilled water until of the consistency of honey and thereafter carefully heated as long as nitrous gases are evolved. Thereafter, it is decanted several times with water and thereafter boiled with strong sodium hydroxide solution for 30 minutes. In this way, a carbon black suitable as developer pigment is obtained in ultra-fine dispersion. 10 5 parts by weight of this carbon black are dispersed in 100 parts by weight of an aqueous solution of wax-free shellac and borax. The solution is prepared by 50 g. of borax and 100 g. of powdered white shellac being allowed to swell in 1 litre of water and being thereafter heated until dissolved.

15 In accordance with the simplest embodiment of the development process, the developer liquid is taken-up with a long-haired broad bristle brush and the brush is moved in one stroke over the previously prepared electrophotographic layer. The developer liquid remains adhering to the charged image areas and after drying, supplied a black, water - resistant reproduction of the exposed original, which reproduction cannot be wiped off. In accordance with another embodiment, a roughened soapstone roller is used for applying the developer liquid, the surface structure of said roller having a mean spacing of the irregularities of about 10 to 500 μ with a depth of 30 to 100 μ . 20

EXAMPLE 9

25 2 g. of the developer pigment prepared according to Example 8 are dispersed in 100 ml. of a 10% aqueous solution of polyvinyl pyrrolidone and is used in this form for wetting the layer provided with an electrostatic charging image. For the production of the aqueous solution, the polyvinyl pyrrolidone obtainable commercially under the name Luviscol K 30 is used. The developer liquid is applied by one of the methods previously described. A deep black colour image is formed, but in contrast to the colour image produced according to Example 8, it can still be washed off. The colour density of the image can be changed in simple manner by diluting the developer solution with water. 30

EXAMPLE 10

35 The electrophotographic material described in Example 8 is developed with the commercially obtainable product of Messrs. Schmincke & Co. "Nanking-Tusche Sorte OO", which is an aqueous carbon black - binder dispersion. The liquid is for this purpose diluted with water in the ratio 2:1 and applied by one of the previously described methods to the prepared electrophotographic layer. It provides a black image of the original which cannot be washed off. 35

EXAMPLE 11

40 The process is performed as described in Examples 8 to 10 with the exception that an aqueous suspension of cobalt aluminate, containing a water - soluble binding agent is used for developing the photo - conductive layer bearing the electrostatic image. The cobalt aluminate paste is diluted with water to obtain a suitable viscosity and the required colour density. The resulting final image is characterised by an excellent fastness to light. 45

The cobalt aluminate of the suspension described above can be replaced with one of the following pigments: Alizarinkrapplack, which is described in the handbook "Technologie der Textulfasern" by Fierz-David, Vol. 3 "Kunstliche organische Farbstoffe" 1926, page 524 *et seq.*, green chromium oxide, sienna, which is a brownish-yellow clay, which is described, for example, in Hackh's Chemical Dictionary, 3.rd Edition, page 769, or cadmium sulphide. 50

In order to make the water image produced by the process of the invention legible, the developer liquid water has added thereto a water - insoluble pigment or dyestuff and a water - soluble binder, which bonds the pigment or dyestuff to the final support after evaporation of the water. Many such aqueous dispersions containing a binder are known in the paint art. The following are to be mentioned as examples: natural or synthetic mineral colours, natural or synthetic organic pigments or dyestuffs or colour lacquers in combination with water - soluble colour binders, such as soluble starches, dextrins, water - soluble alkyl celluloses, carboxymethyl cellulose, gum arabic, tragacanth pectine, agar-agar, alginates, other macromolecular carbohydrates, proteins, bone glues, casein glues, water - soluble plastics such as polyvinyl pyrrolidone, polyvinyl methyl ether, polyvinylalcohol and sodium polyacrylate. 55 60

EXAMPLE 12

100 g. of chemically pure photoconductive zinc oxide (Merck p.a.), 30 ml. of silicone resin, 60% in toluene (for example silicon resin Bayer P 150), 100 ml. of toluene and 25 g. of phenol phthalein are introduced into a ball mill (capacity 1 litre), which is half filled with porcelain balls (1.5 cm. diameter). The mixture is ground for 2 hours and thereafter applied by means of an applicator roller to document paper (100 g./m²) and dried. The thickness of the layer is about 15 μ . The material is now electrostatically charged by means of a corona discharge device at 7 kV, image-wise exposed with incandescent lamp light and developed with 15% sodium hydroxide solution. For the application of the developer liquid, there is employed a roughened soapstone roller, the surface structure of which has a mean spacing of the irregularities of about 10 to 500 μ with a depth of 30 to 100 μ . A reddish-violet image is formed on the white layer.

EXAMPLE 13

The electrophotographic material described in Example 12 is used, but without containing any phenol phthalein. The material is exposed to light in the manner indicated above and thereafter developed with an aqueous acid bromophenol blue solution, which is pale yellow in colour. Thereafter, the developed electrophotographic paper is treated with gaseous ammonia, a bluish-black image being formed. The bromophenol blue can also be replaced by bromocresol green.

EXAMPLE 14

The electrophotographic layer material is prepared by mixing 150 g. of electrophotographic zinc oxide, 100 g. of the polysiloxane resin used in Example 1, 150 ml. of toluene and a dyestuff solution consisting of 0.05 g. of rose bengal in 6.5 ml. of methyl alcohol. A paper support is coated with this mixture and an electrophotographic material is obtained which has a sensitisation maximum in the region of 575 m. μ . The processing is carried out in accordance with Example 12. Formic acid, diluted in the ratio 1:1 with water, is used as developer liquid. The solution bleaches out the sensitising dyestuff at the charged image areas and a negative image of the original becomes visible.

EXAMPLE 15

Example 13 is modified by incorporating 0.02 g. of crystal violet as sensitising dyestuff into the coating material. Development of the layer with hydrazine hydrate (25%) yields a white image on a blue ground.

EXAMPLE 16

100 g. of zinc oxide, 30 ml. of the polysiloxane resin solution (60% in toluene) used in Example 1, 100 ml. of toluene and 10g. of lead acetate are triturated for approximately 2 hours in a ball mill in order to obtain a uniform smooth consistency of the constituents. The mixture is then cast on baryta-coated paper with a layer thickness of about 10 μ and dried. In accordance with the foregoing examples, an electrostatic image is produced on the layer and this is developed with a saturated solution of thioacetamide in 10% sodium hydroxide solution. For applying the developer solution, a rubber roller is employed which is covered with Perlon mesh fabric. The mesh fabric has a thickness of about 50 μ and a mesh size of on average 25 μ . The alkali thioacetamide solution penetrates at the wetted image areas into the layer and reacts with the lead acetate to form a black lead sulphide image. A sodium sulphide solution can be used instead of the thioacetamide solution with equal success.

EXAMPLE 17

The same electrophotographic material as described in Example 13 is used and this is exposed to form an image and developed with an aqueous solution of cobalt chloride. In this way, a practically invisible image consisting of cobalt chloride is obtained. If the image is exposed to gaseous hydrogen sulphide, a deep black reproduction of the subject is obtained.

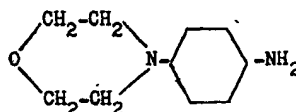
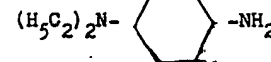
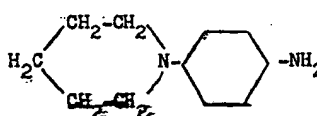
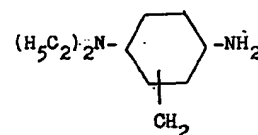
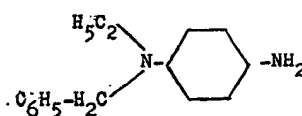
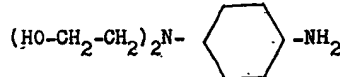
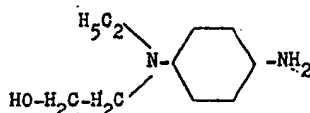
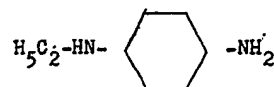
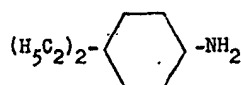
EXAMPLE 18

6 g. of sodium-pyrrolidinodithiocarbamate are added as reaction component to the coating composition according to Example 16 instead of lead acetate and the further processing is carried out in the manner indicated. A development of the electrophotographic layer thus equipped with a 10% aqueous solution of iron ammonium sulphate supplies a dark brown image.

EXAMPLE 19

5 g. of the ZnCl_2 -double salt of diazotised 5 - benzoylamino - 2 - amino - 1,4-hydroquinone diethyl ether are added as reaction component to the coating material according to Example 15 so that electrophotographic material contains both diazo compound and crystal violet. The electro - static charging image is developed by the process described in Example 13, using a 10% α -naphthol solution in sodium hydroxide solution (10%). The coupling reaction of the reaction components in the layer and in the developer solution leads to a bluish black image.

In a manner similar to that indicated above, it is also possible to use the double salts of other diazotised aromatic amino compounds, of which the following are examples:



EXAMPLE 20

An electrostatic charging image is produced on an electrophotographic layer, prepared by applying a mixture of 100 g. of the polysiloxane resin used in Example 1, (60% in toluene), 150 g. of zinc oxide and 160 g. of toluene to aluminium-lined paper. The charging image is thereafter developed by the process described in Example 12 with a solution which is prepared from two parts of a solution of 0.25 g. of diethyl aniline (free from monoethyl aniline) in 200 ml. of sulphuric acid 1:1 and 3 parts of a solution of 2 g. of potassium ferricyanide in 100 ml. of water. A brownish-red image of the original appears on the zinc oxide layer.

EXAMPLE 21

An electrophotographic ZnO -layer as described in Example 1 is charged electrostatically by means of a corona discharge device and exposed to form an image. The

α -naphthol solution described in Example 19 is used as developer and it is applied in the same way. The still moist liquid image is transferred after development to a sheet of paper, which has been coated with a 5% aqueous solution of the diazotised hydroquinone diethyl ether mentioned in Example 19 and thereafter dried. After pulling the two papers apart, the transfer sheet bears a blackish-blue image of the original.

EXAMPLE 22

An electrophotographic ZnO paper as described in Example 1 is treated as in the preceding Example and developed with a 10% aqueous FeCl_3 -solution. After transfer to a paper impregnated with saturated alcoholic gallic acid, a black image of the original is formed on the transfer sheet.

EXAMPLE 23

An electrophotographic material is used, which corresponds to that used in Example 19, but has an additional content of α -naphthol. The material is processed in accordance with Example 19 and developed with a 10% sodium hydroxide solution. The material becomes alkaline at the wetted zones and thereby initiates the coupling reaction, which leads to a bluish-black dyestuff.

Having thus described our invention we now believe our invention to be capable of numerous variations in methods, apparatus and materials. For example, as well as zinc oxide, all other known inorganic and organic photo conductive substances can be used e.g. cadmium sulphide, selenium, sulphur, arsenic trisulphide, lead iodide, lead chromate, cadmium iodide, mercury iodide, aluminium iodide, and also anthracene, anthraquinone, acenaphthene, chrysene, p - diphenyl - benzene, benzanthrone, 1,5-dicyanonaphthalene, 1,4 - dicyano - naphthalene, aminophthalodinitrile, nitrophthalodinitrile, as well as photoconductive azomethines, oxazolones, oxodiazoles, triazoles, imidazolones, imidazolthiones, and in addition polyvinyl carbazoles or other polymeric substances having simultaneously film forming properties.

The invention can also be employed for the development of electroradiographic images. The latent electrostatic image to be developed is in this case produced by means of a xero-radiographic material known per se, the photoconductive layer of which contains for example selenium, zinc oxide, lead iodide or cadmium sulphide sensitive to X-rays.

Furthermore, it is possible to use the process according to the invention for the development of those electrophotographic images which have been recorded on insulating foils.

WHAT WE CLAIM IS:—

1. A process for the production of electrophotographic images wherein a supported photoconductive layer is charged and exposed to an object so as to form a latent electrostatic image which is developed by bringing the entire layer into contact with an aqueous developer composition having electric and wetting characteristics such that the charged areas are wetted by the composition while the uncharged areas repel it.

2. A process as claimed in claim 1, wherein the aqueous developer has a relaxation time small compared with the developing time, a resistivity less than 10^6 ohms. cm. and a wetting angle of more than 90° at the uncharged areas and less than 90° at the charged areas.

3. A process according to claim 1 where said aqueous developer is an aqueous dispersion of coloured compounds compatible with water.

4. A process according to claim 1 wherein said aqueous developer contains a colourless reaction component for colour forming chemical reaction.

5. A process according to claim 4 wherein said aqueous developer contains a colourless reaction component for colour forming chemical reaction while the compound reaction with said reaction component is present in the photoconductive layer.

6. A process according to claim 1 wherein said photoconductive layer is contacted with said aqueous developer by means of a roller having a screen-like notched surface.

7. A process for the production of electrophotographic images, substantially as described with reference to any one of the Examples.

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